

line 29, change "thus does not exceed" into ~~-, thus, is contained in and does~~

*a3* not exceed the disclosure of--; and

after line 30, add the following:

*a4* --EP 00 34 040 A1 describes a multiplicity of layers, the color of most of them(produced under the standard conditions set forth by Barnes/Ward) although not being specified, is referred to as clear. Examples 16 and 17 of the patent describe a greenish borate-containing layer described as cloudy-dull to non-transparent, and Example 14 describes a layer affording a corrosion protection of only 4 hours.--

Page 6, before line 1, center and insert --SUMMARY OF THE INVENTION--;

line 1, change "It is therefore an object of the" into --The--; still line 1, change "to furnish" into --thus furnishes--;

*a5* after line 3, insert as a new paragraph --The layer according to the invention is  
produced in the absence of any oxidant and is consequently free of hexavalent chromium. This may in particular be seen from the fact that the layer according to the invention is not yellow.  
Even where the yellow coloration and the enhanced corrosion protection is brought about by nothing but Ce(IV), the layer according to the invention affords the desired degree of corrosion protection, even without this very costly and rare addition.--;

lines 16-25, delete in their entireties; and

*a6* line 26, after "In" add one preferred embodiment, upon--

Page 7, line 7, change "drawing, wherein" into --drawings--;

after line 7, insert centered --BRIEF DESCRIPTION OF THE DRAWINGS--;

lines 7, 8, 10, 13, 15 and 20; change "Fig." into --Figure--;

lines 9, 12, 14, 15 and 19, change "semicolon" into a period;

lines 16 and 21, change "Figs." into --Figures--;

lines 20-21, delete in their entireties; and

lines 22-26, delete in their entireties.

Page 8, lines 1-23, delete in their entireties;

after line 23, insert centered "DESCRIPTION OF THE PREFERRED EMBODIMENTS"; and

line 24, add "The" before "chromate".

Page 11, line 1, change "Fig. 38 (originally illustration 1)" into "The following

Table 1 provides an evaluation of a depth profile analysis of Figures 5 to 36.

Table 1: Computer Simulation of Kinetic Model of Chromate Coating of Zn for Various Rate Constants

	Methods							
	Ellipsometry nm	SEM nm	Glow-discharge nm (Cr > 1%)	Spectrometer with Cr (%)	Chromium Index	nm (Cr > Zn)	nm (Cr > 30%)	Sample No.
1. Prior Art (Chromititation)								
Yellow Cr(III) + CR(VI)	-	300	440	11	48	17	25	9
Blue CR(III)	98	60	60	8	5	0	0	8
2. Invention (Chromititation)								
60°C Cr(III)	432	300	344	7	23	2	15	1,2,3,4,
100°C Cr(III)	595	-	358	10	38	22	28	6
60°C on Zn/Fe CR(III)	-	-	282	6	16	0	16	7
100°C two-fold [Cr(III)]	953	-	-	-	-	-	-	

Page 13, line 7, after "2 and 3" add "--below--"; and

lines 8-27, delete in their entireties.

Pages 14-15, delete in their entireties.

Page 16, lines 1-4, delete in their entireties;

lines 5-6, change "the enumeration according to claims 9 and 11" into --

ligands of the chromium(III) complex selected from the group consisting of chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and further chelate ligands such as acetylacetone, urea, urea derivatives, and further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur ( $-NR_2$ ,  $-PR_2$ , wherein R independently is an organic, in particular aliphatic radical and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H); phosphinates and phosphinate derivatives; as well as suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and  $H_2O$  and/or the method is performed repeatedly on the surface to be passivated.--; and

line 21, change "By the present invention it is for the first time made possible" into ~~The present invention makes it possible for the first time.~~

Page 17, line 1, change "Moreover yellowish" into --Yellowish--;

lines 4-6, change "the applicant - one of the leading enterprises in the field of surface technology is not aware of any" into --there are no known--; and

lines 8, 10, 13 and 20, change "Fig." into --Figure--.

Page 18, lines 1, 6, 9 and 17, change "Fig." into --Figure--;

line 12, change "Based on the" into --The--;

lines 12-13, change "it therefore results" into --shows--; still line 13, after "like" add "those obtained--;

line 14, add a comma after "however"; and

lines 20 and 24, change "Figs." into --Figures--.

Page 19, line 3, change "It is worth mentioning that a" into --A--; still line 3, change "of" into --in accordance with--;

lines 5-6, change ", whereas even the" into --. In contrast, even a --;

line 19, insert ~~of the above referenced patent~~ after "transparent";

line 22, delete "In", and after "040" insert --describes--; still lines 22-23, delete "is described";

line 27, change "only present" into --present only--; and still line 27, start new paragraph with "the layer according to".

Page 20, line 1, insert --of EPO 00 34 040-- after "17"; and

lines 21, 27 and 30, change "Fig." into --Figure--.

Page 21, lines 1 and 3, change "- prior art -" into --of EP 00 34 040--;

line 10, change "Fig." into --Figure--; and

line 30, change "Figs." into --Figures--.

Page 22, line 1, change "The following Table" into --Table 2 below--;

lines 1-2, change "calibration is valid:" into --the calibration is valid.--;

before the table, insert centered --Table 2: Concentration Range for Calibration--;

in the line between tables, change "following Table:" into --results in the following Table 3.--; and

before the second table, insert centered --Table 3: Samples' Information--.

Page 23, line 1, after the table, change "Fig." into --Figure--; and

after line 3, insert **EXAMPLES.**

### **Example 1: Coating of Zinc Coated and Galvanized Steel Pieces**

Small steel pieces were bright-zinc coated electrolytically (approx. 15  $\mu\text{m}$ ) and, following galvanization, singly immersed for 30 seconds in a boiling (approx. 100°C) aqueous solution containing the following components:

100 g/l  $\text{CrCl}_3 \cdot \text{H}_2\text{O}$  (trivalent chromium salt),  
100 g/l  $\text{NaNO}_3$ ,  
15.75 g/l NaF, and  
26.5 g/l citric acid · 1 aq.

The solution had previously been adjusted to pH 2.5 with sodium hydroxide solution. The parts were then rinsed with water and dried in an air flow. A greenish, strongly iridescent layer comprising

all  
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zinc/chromium oxide formed on the pieces. The sample was subjected to a corrosion test in a salt spray cabinet according to DIN 50021 SS. It was surprisingly found that the chromate layer formed presented excellent corrosion protection until the appearance of first corrosion products of 1000 hrs. according to DIN 50961, Chapter 10, in particular Chapter 10.2.1.2.

The novel greenish chromate layer had a layer thickness of approx. 800 nm and was produced by a process not involving any chromium(VI) and could be proven to be chromium(VI)-free. The production method for the novel, greenish chromium(VI)-free chromation described above is not very economical for use in conventional plants, due to the relatively high temperature required by the process solution. Further theoretical considerations concerning chromium(VI)-free chromate coatings, and further trials, finally resulted in far more economical production conditions.

#### **Example 2: Coating of Zinc Coated Steel Pieces**

Electrolytically bright-zinc coated (15  $\mu\text{m}$ ) steel parts were immersed for 60 sec. in an aqueous chromate coating solution containing

50 g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  (trivalent chromium salt),  
100 g/l  $\text{NaNO}_3$ , and  
31,2 g/l malonic acid.

the pH of which having been previously adjusted to 2.0 with sodium hydroxide solution. The samples were then rinsed and dried, and subjected to a corrosion test in a salt spray cabinet according to DIN 50021 SS. The sample exhibited a corrosion protection of 250 hrs. until first attack according to DIN 50961.

Malonic acid is a ligand enabling more rapid ligand replacement kinetics at the chromium(III) than the fluoride of Example 1. Good corrosion protection, by far exceeding the minimum requirement of DIN 50961 for Method Group C (yellow chromation), may thus already be achieved at 60°C.

**Example 3: Coating of Zinc Coated Steel Pieces**

Electrolytically bright-zinc coated (15  $\mu\text{m}$ ) steel parts were immersed for 60 sec. in an aqueous chromate coating solution consisting of

- 50 g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  (trivalent chromium salt),  
3 g/l  $\text{Co}(\text{NO}_3)_2$ ,  
100 g/l  $\text{NaNO}_3$ , and  
31.2 g/l malonic acid,

previously adjusted to pH 2.0 with a sodium hydroxide solution. The samples were then rinsed and dried, and subjected to the same corrosion test in the salt spray cabinet according to DIN 50021 SS. The samples exhibited a corrosion protection of 350 hrs. until first attack according to DIN 50961.

Cobalt is an element which is capable, in accordance with the invention, of catalyzing ligand replacement and reducing reverse reaction II by insertion of kinetically stable oxides into the chromate layer. The thus produced chromate layer is thus thicker. The concept advanced by the present inventors has, thus, been experimentally verified. Corrosion enhanced protection was compared with Example 3 by the sole addition of Cobalt into the chromate coating solution.

Novel greenish chromate layers were also produced on zinc surfaces as described in Example 2, except that the temperature was 40, 60, 80 and 100°C. The thicknesses of the respective chromate layers were determined by RBS (= Rutherford-Backscattering) testing. The corresponding corrosion protection values in hours of salt spray cabinet exposure according to DIN 50021 SS until first attack according to DIN 50961 Chapter 10 are listed in Table 4 below.

**Table 4: Corrosion Protection Values**

J/ °C	Thickness / nm	Corr. Prot. / hrs.
40	100	50-60
60	260	220-270
80	400	350 450
100	800	800-1200

all cont  
Depending on the complex ligands used, e.g. malonate in Examples 2 and 3, it is possible to achieve even considerably higher layer thicknesses and corrosion protection values. Complex ligands containing nitrogen, phosphorus or sulfur as the complexing functional group, e.g.  $-NR_2$ ,  $-PR_2$ , wherein R independently is an organic, in particular aliphatic radical, and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H, are also used in embodiments of this invention. With these ligands, it is possible to produce the excellent indicated layer properties (within limits) even at room temperatures.

#### **Example 4: Zn/Fe Alloy Coated Steel Pieces**

Steel pieces electrolytically coated with a zinc/iron alloy (0.4-0.6% iron) were immersed for 60 sec. at 60°C in the following aqueous chromate coating solution:

50g/l  $CrCl_3 \cdot 6 H_2O$ ,

100g/l  $NaNO_3$ ,

31.2 g/l malonic acid,

and adjusted beforehand to pH 2.0 with NaOH. The pieces were rinsed and dried, and exhibited a transparent, greenish, slightly grey, strongly iridescent layer on the zinc/iron. When tested in the salt spray cabinet in accordance with the above specified DIN and ASTM standards, the coated pieces exhibited a corrosion protection of 360 hrs. until first attack (according to DIN 50961).

#### **Example 5: Coating of Zinc/Ni Alloy Coated Steel Pieces**

Steel parts electrolytically coated with a zinc/nickel alloy (8-13% nickel) were immersed for 60 sec. at 60°C in the following aqueous chromate coating solution:

50g/l  $CrCl_3 \cdot 6 H_2O$ ,

100g/l  $NaNO_3$ , and

31.2 g/l malonic acid,

and adjusted to pH 2.0 with NaOH. Following rinsing and drying, a transparent, greenish, dark-grey, strongly iridescent layer became visible on the zinc/nickel surfaces. When tested in the salt spray